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14. ABSTRACT
Centimeter-size KBBF and RBBF single crystals have been grown hydrothermally for NLO applications. Second harmonic generation of 800 nm fundamental light has been demonstrated using both KBBF and RBBF in preliminary studies.

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Hydrothermal Growth and Properties of $KBe_2BO_3F_2$ (KBBF) and $RbBe_2BO_3F_2$ (RBBF) Single Crystals

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Abstract: Centimeter-size KBBF and RBBF single crystals have been grown hydrothermally for NLO applications. Second harmonic generation of 800 nm fundamental light has been demonstrated using both KBBF and RBBF in preliminary studies.

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1. Introduction

Alkali fluorberyllium borates such as $KBe_2BO_3F_2$ (KBBF) and $RbBe_2BO_3F_2$ (RBBF) are fascinating materials offering nonlinear optical (NLO) capabilities over a very broad range of wavelengths well into the deep-UV [1]. Flux grown KBBF single crystals are particularly well-studied [2,3] and a number of elegant NLO experiments have recently been performed using these crystals. KBBF has proven to be versatile in the visible region, offering efficient sum frequency mixing over the 397-539 nm range [4], as well as the UV and deep-UV regions where it has been used with a prism coupling technique to efficiently generate 266 nm light [5] and several other sub-200 nm wavelengths [6,7], even as low as 156 nm [8]. However, the crystal growth process has proven to be both difficult (crystals are typically grown to only a few mm in thickness) and costly, limiting the mainstream availability of suitable crystals [9]. Hydrothermal growth methods have only recently been pursued as an alternative method to obtain thicker KBBF crystals [10,11], and optical data on these crystals has not yet been reported. So far, RBBF has been relatively unexplored despite its identical structure to KBBF [11,12]. Here, we overview the hydrothermal growth of KBBF and RBBF and present some preliminary optical characterization of these interesting materials.

2. Experimental

KBBF and RBBF crystals were grown hydrothermally in silver lined autoclaves by direct recrystallization of polycrystalline feedstock onto seed crystals using fluoride mineralizers. The feedstock materials were prepared at 700 °C by stoichiometric solid state reactions of KBF_4, BeO and H_3BO_3 for KBBF and Rb(OH), BeO, B_2O_3 and NH_4F for RBBF. Seeds were obtained from spontaneous nucleation experiments and suspended from a silver ladder which was placed in the autoclave along with the appropriate feedstock and aqueous KF or RbF mineralizers (1 M concentrations). The region of the autoclave containing the feedstock was heated to 400-450 °C, and the region containing the seed crystals was held 20 degrees cooler. This heating arrangement was maintained for 4-6 weeks until the autoclave was cooled to room temperature and the as-grown crystals were retrieved.

Second harmonic generation from the resulting crystals was characterized using a Tsunami laser (Spectra Physics) having a fundamental beam of 800 nm, 200 fs pulse width, 8 MHz repetition rate and pumped by a 9 W Millenia laser (Spectra Physics). The fundamental beam was focused onto the single crystal using an AR lens (f = 50 mm). The second harmonic beam was separated using a short pass filter and its power was measured using a calibrated GaP detector (FGAP71 – Thorlabs). Angle tuning was performed at 150 mW fundamental power to optimize the intensity of the second harmonic.

3. Results and Discussion

KBBF and RBBF crystals have been grown hydrothermally having dimensions over 1 cm on (001) and approximately 4 mm thick. Representative crystals are shown in Figure 1 and were grown with a dissolution (feedstock) zone temperature of 410 °C with the temperature gradient applied as described above. Optically clear growth was observed and growth rates for the crystals pictured in Figure 1 were 0.75 mm/week on (001) and 0.36

mm/week in thickness for KBBF and 0.70 mm/week on (001) and 0.46 mm/week in thickness for RBBF. Both crystals formed as hexagonal plates, but the KBBF crystal did not reach its finished morphology since the seed crystal began as only a plate fragment in this experiment.

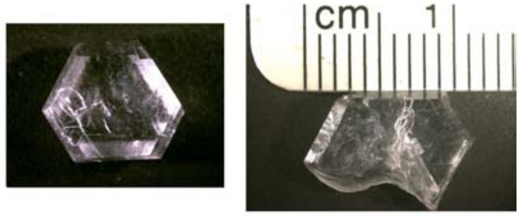

Fig. 1. As-grown RBBF (left) and KBBF (right) crystals.

SHG from the 800 nm fundamental beam was observed as an intense blue light after passing through the target crystal. Intensity of the second harmonic beam increased with increasing fundamental power with no observed power quenching up to 450 mW, as shown in Figure 2. The KBBF (1 mm thick) and RBBF (0.6 mm thick) single crystals in these preliminary studies showed comparable second harmonic intensities despite their differing thicknesses. This is encouraging given the propensity of RBBF to form thicker, less micaceous single crystals.

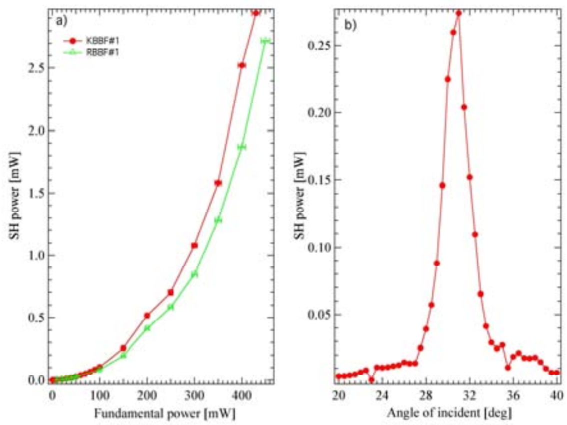

Fig. 2. Second harmonic generation using KBBF (red) and RBBF (green) – a) power curve (left) and b) angle tuning at 150 mW (right).

4. Conclusions

KBBF and RBBF crystals have been grown hydrothermally to sizes exceeding 1 cm. Preliminary optical characterization has been performed on thin crystals. KBBF and RBBF performed comparably and showed no signs of power quenching up to 450 mW. Detailed optical transparency and SHG experiments at other wavelengths are currently underway using thicker crystals.

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